

Electric Field Induced Strains in Electroactive Polymers  
Under High Hydrostatic Pressure –  
System Development and Material Characterization

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<b>14. ABSTRACT</b>  This program has been used to support the training of a graduate student, Steve Gross, in the area of (i) developing a high performance piezo-bimorph based dilatometer which can be used to characterize the electric field induced strain response in polymer films under high hydrostatic pressure, (ii) using the set-up developed to evaluate the field induced strain performance in high energy electron irradiated P(VDF-TrFE) copolymer. As a result of this program, a unique dilatometer, which has a sub-angstrom resolution and can be used under high hydrostatic pressure was developed. The study of the field-induced strain under high hydrostatic pressure showed that the high energy electron irradiated copolymer has a very high load capability and can maintain the high strain level to more than 1000 psi pressure. Under the support of this program, Mr. S. Gross has completed his MS degree and is currently pursuing his Ph.D. at the Electrical Engineering Department of Penn State University.						
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This program has been used to support the training of a graduate student, Steve Gross, in the area of (i) developing a high performance piezo-bimorph based dilatometer which can be used to characterize the electric field induced strain response in polymer films under high hydrostatic pressure, (ii) using the set-up developed to evaluate the field induced strain performance of high energy electron irradiated P(VDF-TrFE) copolymer. Under the support of this program, Mr. S. Gross has completed his MS degree and currently he is pursuing Ph. D. at the Electric Engineering Department of Penn State University.

## **Introduction**

Electroactive polymers for actuators and transducers offer many advantages over traditionally used piezoceramics. Polymeric materials are in general easily processed into complex shapes and thin films, resistant to mechanical shock, and posses a low density and an acoustic impedance similar to that of water or human tissue. However, their wide spread adoption in devices has been seriously hindered by their comparatively low electroactive response. This shortcoming has been greatly alleviated by the remarkably high strain ( $>5\%$ ), and elastic energy density observed in electron-irradiated Poly(Vinylidene Fluoride-Trifluoroethylene) copolymer [1]. The successful exploitation of this class of materials demands that the electric field induced strain be fully characterized under various load conditions, which would be encountered in normal operating environments. Of particular interest, is the adoption of this novel material in under-water acoustic transducers for sonar applications. Therefore, the strain behavior parallel to the applied electric field and the electro-mechanical coupling modulus at elevated hydrostatic pressures require evaluation. To achieve this, a fully automated, high-resolution dilatometer system capable of subjecting polymer samples to elevated hydrostatic stresses has been developed.

## **The Dilatometer System**

Depicted in figure 1, is the completed experimental apparatus showing an enlargement of the strain sensor located within a pressurized tank.

The current tank is rated up to 1200 psi (8.4MPa), but can be easily modified to attain higher pressures. The sensor's design is based on a piezoceramic bimorph mounted as a cantilever

with a metal stylus fixed to the free end [2]. The stylus rests on the polymer sample applying a minimal amount of contact pressure. A strain in the sample results in a displacement at the free end of the bimorph that in turn generates an electric charge proportional to the strain.

$$q(t) = -\frac{3d_{31}(h^2 + 2Lh)}{8t^2 B} \Delta(t), \quad (1)$$

where  $q$  is the charge,  $\Delta$  is the displacement of the stylus,  $B$  is a geometric parameter,  $h$  is the length of the piezoceramic bimorph,  $L$  is the length of the stylus, and  $d_{31}$  is the piezoelectric coefficient. Using a charge amplifier or integrator, the sample strain is made proportional to the output voltage. This voltage is measured using a lock-in amplifier. An Omega pressure transducer that is interfaced with a PC measures the pressure in the tank.

Due to numerous advantages, a fully automated data acquisition system based on National Instruments' labVIEW package was incorporated with the dilatometer. Four virtual instruments (VIs) were custom written to provide measurement and control solutions. The *strain response* and *frequency response* VIs were developed to measure and record the output from the sensor as the driving field or frequency is varied.

Calibration of the instrument was performed using an aged PZT-5H standard. Although quartz could have been used to minimize the nonlinear effects in the standard, a large strain was required to properly prove the dilatometer in the range of strain required by the polymer of interest. The error resulting from the PZT standard at these field levels ( $\sim 50\text{V/cm}$ ) is about 0.5% and its use is therefore justified [3]. Since the instrument is used at elevated pressures, the calibration was performed in-situ, and the results are shown in figure 2. Since the piezoelectric coefficient can be considered a constant over the range of pressure used in this investigation [4], the 14% decrease in sensitivity (slope) at 1200 psi can be attributed to the sensor itself. The sensitivity factor of the dilatometer is then,

$$\beta = \frac{\Delta}{V_{out}} = \frac{d_{33} V_{sample}}{V_{out}} \quad (2)$$

where  $V_{out}$  and  $V_{sample}$  are respectively the voltage output from the sensor and voltage applied to the sample. The sensitivity factor is inversely proportional to the slope of the curve in figure 2.

### Instrument Performance

To evaluate the system's frequency response, the ceramic standard was excited while submersed in hydraulic oil and the resulting voltage output was measured, as the frequency was linearly increased. The data shows a flat response up to one kilohertz, and although these results prove the instrument up to this limit, induced flexural modes in a compliant material such as this polymer, may reduce the usable frequency range.

An instrument's resolution can be defined as the smallest change in the measurand (input parameter) that can be discerned. To evaluate the dilatometer's resolution, the *strain response* VI was employed to decrement the driving voltage applied to the standard while the system noise was measured at each strain level. Figure 3 shows the ideal piezoelectric behavior as the dashed curve passing through the origin. Since the shaded region represents the system noise, the point at which the output signal is completely obscured by the noise is the instrument's resolution. Alternatively, the resolution is the point at which the signal to noise ratio (SNR) reaches zero. At a driving frequency of 10 Hz and a lock-in effective noise bandwidth (ENBW) of  $\sim 8\text{mHz}$ , figure 3 shows the resolution to be  $2 \times 10^{-3}$  angstroms ( $\text{\AA}$ ).

Because the instrument's resolution is ultimately a function of the system noise, an analysis of the noise sources and mechanisms was conducted [5]. The lock-in input noise is negligible and was ignored in the analysis. Using low noise coaxial cable and a proper layout, external interference was minimized. A noise model for system is shown in figure 4a, with  $C_o$  and  $C_f$  being respectively the sensor's capacitance and amplifier's feedback capacitance. The internal noise sources selected in the analysis were: the thermal noise associated with the dielectric losses in the piezoelectric bimorph  $E_s$ , and the charge amplifier's voltage ( $E_A$ ) and current noise ( $I_A$ ).

$$\begin{aligned} E_{total}^2 &= E_{os}^2 + E_{oA}^2 + E_{oIA}^2 \\ &= \frac{4kTD}{\omega C} + 4E_A^2 + \frac{I_A}{\omega C} \end{aligned} \quad (3)$$

In the above equation,  $E_o$  represents the voltage output due to each source, D is the dissipation factor or  $\tan\delta$ , k is Boltzman's constant,  $\omega$  is the angular frequency, and  $C=C_o=C_f$ . The total calculated system noise arising from these three uncorrelated sources shows a  $1/f$  spectrum with the amplifier voltage noise being the dominant offender (figure 4b).

Armed with an understanding of the system's noise mechanisms and characteristics, the noise spectrum was measured using the *frequency response VI* from 2 to 100 Hz for the two conditions of the sensor connected and disconnected. Although the noise from the charge amplifier alone (sensor disconnected) agrees well with the predicted value, the measured noise level of the complete system is twice as predicted. This discrepancy can be attributed to mechanical vibrations in the supporting structure being converted to electrical noise by the sensor. Often times, very sensitive measuring instruments employ sophisticated vibration isolation equipment and techniques to reduce this mechanical noise. Although several techniques were adopted and effective, the mechanical noise is still the dominant factor in limiting the resolution. In principle, the ultimate resolution of this dilatometer can be extrapolated from the calculated system noise to be on the order of  $10^{-4}\text{\AA}$  at 10 Hz and the conditions described above.

### Results and interpretation

With the system calibrated a series of experiments were undertaken to fully characterize the electric field induced strain behavior of P(VDF-TrFE) copolymer as a function of hydrostatic pressure. Test samples were prepared from 65/35 mol %, 40 mm film electron-irradiated at 95 °C with a dose of 60 Mrad. Circular gold electrodes, approximately 4mm in diameter, were sputtered on each side and the excess polymer was trimmed off to avoid flapping of the edges. With a sample in the tank, the pressure was raised to 1200 psi (8.3 MPa) and with the *strain response VI* the applied electric field was varied from zero to 74 MV/m and back to zero. The strain level was recorded with increasing and decreasing field and the average values for various tank pressures is shown in figure 5. The electric field related electrostrictive coefficient M, defined as  $S_3=M_{33} E_3^2$ , where S is the strain and E is the electric field, is also displayed for various pressures in figure 5. The figure clearly shows a small, but observable increase in the

strain of about 17% at the highest field and pressure levels. The electrostrictive coefficient shows a similar dispersion with pressure. Further tests confirm this behavior.

The induced strain in the direction perpendicular to the applied field was measured using a separate, specially developed apparatus [6]. This instrument was designed to measure the generated transverse strain in freestanding polymer films while applying a static tensile stress in the transverse direction. Samples were prepared from copolymer film initially stretched (stretch ratio = 5) then treated under the conditions described above. The behavior of the electrically induced strain under various static tensile loads is shown in figure 6. The curves indicate that as the load is increased under a constant electric field, the resulting strain increases to a maximum and then begins to decrease.

The results obtained show conclusively that the electrically induced strain in P(VDF-TrFE) copolymer has a high load capability and can be operated at an elevated hydrostatic pressure or transverse load without losing strain level. The small increase in the strain with hydrostatic pressure or transverse load is an indication that the induced strain response in the polymer is a result of a local transformation of the non-polar phase to a polar phase. It provides credence that this phenomenon is truly electrostrictive and does not arise solely from the Maxwell Stress effect.

To understand this small change with the stress, and to simplify the analysis, we adopt the Smolenskii model of a relaxor ferroelectric that describes the material as having a broad distribution of Curie transition temperatures. From the Landau-Devonshire theory, it can be shown that an applied stress will cause a shift in the local Curie temperature by an amount,

$$\Delta T_c = 2\epsilon_0 C Q_{i3} X_i$$

where  $T_c$  is the Curie temperature,  $C$  is the Curie-Weiss constant, and  $Q_{i3}$  is the polarization related electrostrictive coefficient. For P(VDF-TrFE) copolymer, the hydrostatic electrostrictive coefficient ( $Q_h = Q_{33} + 2Q_{13}$ ) is negative due to the fact that the polar phase has a smaller unit cell volume compared with that of the non-polar phase. Taking as convention that

a tensile stress is positive, an increase in the hydrostatic pressure will cause an upward shift of the local Curie temperature. In other words, for the electrostrictive P(VDF-TrFE) copolymer, an increase in hydrostatic pressure is equivalent to a drop in temperature. Other experiments not yet published have shown that a lowering of the temperature below room temperature will result in an increase of the field-induced strain. Therefore, it was expected that the field-induced strain would show a similar increase with hydrostatic pressure in the pressure range investigated. Likewise, since  $Q_{13}>0$ , a tensile stress in the stretched direction causes an increase in the local transition temperature accompanied by an increase in the strain response. Based on this theory, it is expected that the strain response should begin to decrease as the hydrostatic pressure is raised beyond 1200 psi.

## **Summary**

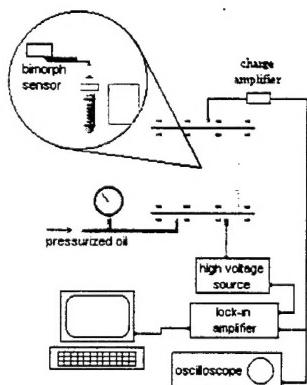
A fully automated dilatometer has been developed to evaluate the electric field induced strain response in soft polymer thin films at elevated hydrostatic pressures. The system was demonstrated to a poses a resolution of  $2\times10^{-3}\text{ \AA}$  at 10 Hz and through a noise analysis it was determined that this figure could be improved by an order of magnitude. Using the calibrated instrument, the strain behavior of the irradiated P(VDF-TrFE) copolymer has been characterized under hydrostatic stress. The results show that this enhanced material has a high load capability. In addition, the small increase in strain with pressure indicates that the strain response is due to the local phase transformation from a non-polar to a polar phase.

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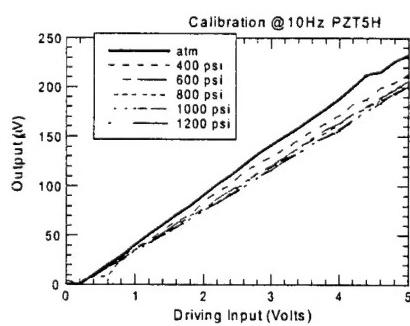
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### Figures:



*Figure 1:* Experimental apparatus including the dilatometer, supporting instrumentation, and data acquisition hardware



*Figure 2* Calibration of the dilatometer at elevated hydrostatic pressures

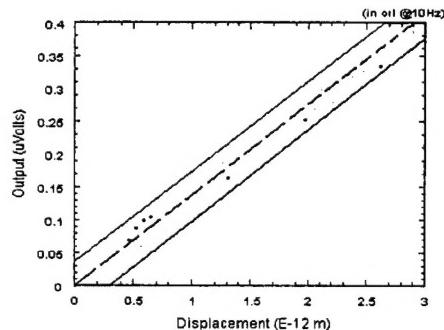


Figure 3 Instrument's resolution measured at 10 Hz. Dashed line represents ideal piezoelectric behavior

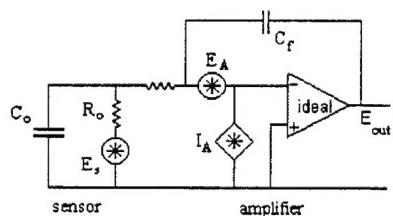


Fig. 4(a) Figure 4 System noise model

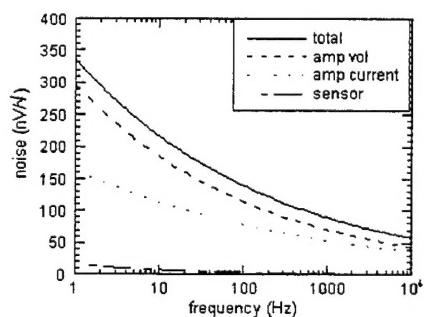


Figure 4(b) Calculated noise spectrum due to internal sources

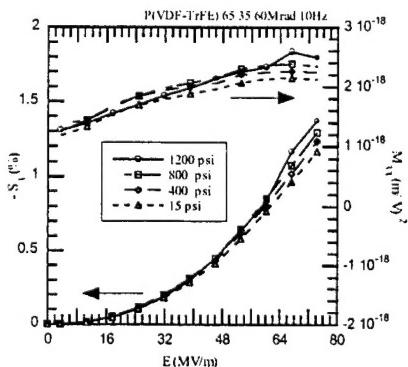
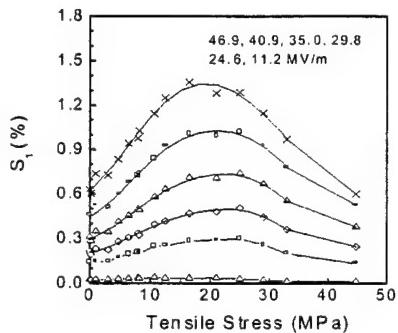


Figure 5 The electrostrictive strain and coefficient as a function of applied field measured at various hydrostatic pressures.



*Figure 6* Transverse strain as a function of tensile stress  $T_1$  at various electric fields

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2. Vivek Bharti, Z-Y Cheng, S. Gross, T. B. Xu, and Q. M. Zhang. High Electrostrictive Strain under High Mechanical Stress in High Energy Electron Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer Films. *Appl. Phys. Lett.* 75, 2653-2655 (1999).
3. S. J. Gross, V. Bharti, Z-Y. Cheng, and Q. M. Zhang. Mechanical Load Effects on the Electrostrictive Strain of P(VDF-TrFE) Copolymer. Proc. 1999 IEEE Inter. Symp. Ultrasonics, 1019-1023 (Lake Tahoe, NE, 1999).

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2. S. J. Gross and Q. M. Zhang. Mechanical Load Effects on the Electrostrictive Strain of P(VDF-TrFE) Copolymer and the Development of a High-Resolution Hydrostatic-Pressure Dilatometer. 1999 US Navy Workshop on Acoustic Transduction Materials and Devices (April, 1999, Penn State University).

3. Z. Y. Cheng, S. Gross, V. Bharti, T. B. Xu, Q. M. Zhang. Electromechanical Properties of Relaxor P(VDF-TrFE) Copolymers. MRS 1999 Fall Meeting, Boston, November 29, 1999.
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# **Appendix**

The Pennsylvania State University

The Graduate School

Department of Electrical Engineering

**THE DEVELOPMENT OF A HIGH RESOLUTION HYDROSTATIC  
PRESSURE DILATOMETER AND THE PRESSURE EFFECTS ON  
THE ELECTROSTRRICTIVE STRAIN OF POLY(VINYLDENE  
FLUORIDE) TRIFLUOROETHYLENE COPOLYMER**

A Thesis in

Electrical Engineering

by

Steven Joseph Gross

Submitted in Partial Fulfillment  
of the Requirements  
for the Degree of

Master of Science

August 1999

## ABSTRACT

Electroactive polymers for actuators and transducers offer many advantages over traditionally used piezoceramics. Polymeric materials are in general easily processed into complex shapes and thin films, resistant to mechanical shock, and posses a low density and an acoustic impedance similar to that of water or human tissue. However, their wide spread adoption in devices has been seriously hindered by their comparatively low electroactive response. This shortcoming has been greatly alleviated by the remarkably high strain (>4.5%), and strain energy density observed in electron irradiated Poly(vinylidene fluoride-trifluoroethylene) copolymer. The successful exploitation of this material demands that the electric field induced strain be fully characterized under various load conditions, which would be encountered under normal operating environments. The strain behavior of a chosen material at elevated hydrostatic pressures is a critical parameter in the design of under-water acoustic transducers. The dependence of the electromechanical properties as a function of pressure is then of great interest.

To evaluate this dependence, a bimorph-based dilatometer designed to measure the strain parallel to the applied electric field in thin and soft polymer films under hydrostatic pressure has been developed. The instrument has a sub-angstrom resolution and can apply a pressure of 1200 psi (8.3 MPa) to a sample. The frequency range of operation spans from a few mHz to one kHz. To assess the performance of the dilatometer, a detailed analysis of the measuring system's performance has been carried out. The experimental results are consistent with the inherent high sensitivity

characteristics of a bimorph-based dilatometer. The resolution of this instrument has been measured at  $2 \times 10^{-3}$  Å, and is therefore on a par with even the most sensitive laser interferometric systems. Since the degradation of the resolution is primarily caused by the system's noise, an analysis of the noise sources and mechanisms was conducted. The analysis demonstrated that mechanical vibration is the largest culprit of system noise, and that the noise arising from the dielectric losses in the sensor, account for only a small fraction of the system's intrinsic noise. The models also predict that via improved vibration isolation techniques and procedures, the instrument's ultimate resolution can reach on the order of  $10^{-4}$  Å.

Using the newly developed measuring instrument, the field-induced strain along the thickness direction was characterized for electrostrictive P(VDF-TrFE) films. The results show a modest increase in strain response with pressure, up to the instrument limit, indicating the new electrostrictive polymer has a high load capability. From Landau-Devonshire theory, it can be demonstrated that an increase in pressure results in an upward shift of the local Curie temperature. This is equivalent to a lowering of the temperature, which has been shown to increase the strain response in this copolymer.